IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application Inventor(s): S. Brad Herner *et al.* Appl. No.: 10/769,047 Filed: January 30, 2004 Title: LOW TEMPERATURE, LOW-RESISTIVITY HEAVILY DOPED P-TYPE POLYSILICON DEPOSITION	PATENT APPLICATION Art Unit: 1762 Examiner: Chen, Bret P. Docket No. SAND-01138US0 (formerly MA-100-I) **Customer No. 64948**

Assistant Commissioner for Patents
PO Box 1450
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DECLARATION UNDER 37 CFR §1.132

Dear Sir:

As an inventor of the above-captioned application and one skilled in the art of semiconductor fabrication, I, S. Brad Herner, Ph.D., hereby declare my opinion that:

1. If 500 sccm of SiH_4 and 5 sccm of BCl_3 are flowed in a conventional CVD furnace at a deposition temperature of 480°C and a pressure of 70 Pascal (525 mTorr), a silicon film will be produced having a concentration significantly greater than 3×10^{21} boron atoms/cm^3, probably about 5×10^{21} boron atoms/cm^3. This conclusion is based on the data presented in S.B. Herner and M.H. Clark, "Silicon deposition from BCl_3/SiH_4 mixtures: Effect of very high boron

concentration on microstructure," *J. Vac. Sci. Tech. B* 22(1) pp. 1-5 (2004) and in S.B. Herner et al., "Low resistivity p^+ polycrystalline silicon deposition at low temperatures with SiH_4/BCl_3," *Electrochemical and Solid State Letters* 7, G108-G111 (2004).

2. If 500 sccm of SiH_4 and 0.5 to 22.4 sccm of BCl_3 are flowed in a conventional CVD furnace at deposition temperatures between 390 and 450°C, and at pressure of 70 Pascal (~525 mTorr), a silicon film will be produced having a concentration greater than about 4×10^{21} boron atoms/cm^3.

3. In general, as the boron concentration in silicon increases, the resistivity (or specific resistance in Noda et al., US Patent No. 6,905,963) decreases. However, as shown in Herner et al. (JVST B), when boron concentration exceeds 3×10^{21} boron atoms/cm^3, resistivity of *in situ* boron-doped silicon begins to increase again. In table I of Herner et al. (ESSL), the resisivity at various concentrations of boron in silicon are shown:

   $2 \times 10^{20}/cm^3$: 6260 μΩ cm (= 0.00626 Ω cm)

   $7 \times 10^{20}/cm^3$: 4320 μΩ cm (= 0.00432 Ω cm)

   $2 \times 10^{21}/cm^3$: 3260 μΩ cm (= 0.00326 Ω cm)

   Noda et al. show the specific resistance (resistivity) of their boron-doped silicon films in Figure 9, with most films around ~7.5 Ω cm. The resistivities shown in Fig. 9 indicate that the Noda et al. films have boron concentration either less than

$1 \times 10^{20}/cm^3$ or greater than $6 \times 10^{21}/cm^3$, as extrapolated from Figure 3 of Herner et al. (JVST B paper)

4. All statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true. Further, these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful statements may jeopardize the validity of the application or any patent issuing therefrom.

Respectfully submitted,

Scott Brad Herner
S. Brad Herner, Ph.D.

April 24, 2007
Date

EXHIBIT A

Silicon deposition from BCl_3/SiH_4 mixtures: Effect of very high boron concentration on microstructure

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The microstructures of *in situ* boron-doped silicon films deposited by low-pressure chemical vapor deposition using SiH_4 and BCl_3 source gases on SiO_2 substrates have been characterized. As-deposited films have a decreasing sheet resistance with increasing boron concentration up to $3.1\pm0.6\times10^{21}/cm^3$, and are polycrystalline. As the boron concentration exceeds $3.1\pm0.6\times10^{21}/cm^3$, the sheet resistance increases dramatically. It is shown that as the boron concentration in the silicon film exceeds $3.1\pm0.6\times10^{21}/cm^3$, the films transition from a completely polycrystalline phase to a combination of polycrystalline and amorphous phases as deposited. The amorphous phase has a higher boron concentration than the polycrystalline phase, as shown by selective Auger electron spectroscopy and secondary ion mass spectrometry. The relative fraction of amorphous phase can be controlled by boron concentration. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1631292]

I. INTRODUCTION

Thin silicon films have many applications for integrated circuits: As a gate, line resistor, and local interconnect in complementary metal–oxide–semiconductor transistors; as a source, channel, or drain in thin film transistors.[1,2] Ion implantation is the preferred method to dope silicon films after deposition due its ability to be area selective (in conjunction with photolithography). There are applications in which it is economically or technically advantageous to dope the silicon during deposition. *In situ* doping removes the need for ion implantation, as well as the screen oxide deposition and etch often associated with ion implantation, thus eliminating costly steps from the wafer fabrication process. *In situ* doping provides dopant concentration depth profiles with steep gradients beneath the silicon surface that cannot be achieved with ion implantation.[3] Recently, the use of *in situ* doped silicon has been expanded by the development of memory devices that can be stacked on top of one another, extending device densities into three dimensions.[4,5]

Low-pressure chemical vapor deposition (LPCVD) is the preferred method for commercial deposition of silicon films due to its high throughput, relatively simple equipment, and compatibility with other common silicon processes. A variety of gas sources have been used to achieve both *p*- and *n*-type *in situ* doping for silicon LPCVD. The addition of the dopant gases to the silicon source gas has been observed to change the nature of the deposition. Specifically, the rate of deposition, the uniformity of deposition across a wafer surface, nucleation upon nonsilicon surfaces, such as SiO_2, and finally crystallinity of the deposited silicon film, can all be affected by the addition of dopant gases. Silicon films can be deposited in an amorphous or polycrystalline phase depending on deposition temperature, as well as other deposition conditions. Dopant gases such as diborane (B_2H_6) have been shown to decrease the transition temperature of silicon films, the temperature at which the film goes from being deposited amorphous to being deposited polycrystalline.[6–10] In contrast, very large incorporation of boron has been observed to cause silicon films to revert to being polycrystalline as deposited with lower boron concentrations to partially amorphous state as deposited.[10]

We characterize the deposition rate, sheet resistance, boron incorporation, and crystallinity of silicon films doped *in situ* with boron trichloride (BCl_3). At a deposition temperature of 550 °C and a pressure of 400 mTorr, thin films deposited on SiO_2 with a boron concentration less than $6.0\pm1.2\times10^{19}/cm^3$ were amorphous. Films deposited on SiO_2 with a boron concentration between $6.0\pm1.2\times10^{19}/cm^3$ and $3.1\pm0.6\times10^{21}/cm^3$ were entirely polycrystalline. Films deposited on SiO_2 with boron concentrations greater than $3.1\pm0.6\times10^{21}/cm^3$ had both amorphous and polycrystalline phases. We propose a mechanism for the crystallinity of the silicon films deposited on SiO_2 with a boron concentration greater than $3.1\pm0.6\times10^{21}/cm^3$ that is consistent with the observations. This model is based on a maximum concentration of boron that can be incorporated in the silicon grains and grain boundaries compared with amorphous silicon.

II. EXPERIMENTAL METHODS

Silicon films were deposited on 200 mm silicon wafers with 100 nm of thermally grown SiO_2. The deposition tool was a vertical furnace capable of holding 80 wafers with a pitch of 8.6 mm in a quartz boat. The boat was rotated, and a full load of wafers was maintained during each deposition. Good deposition uniformity was achieved by differential

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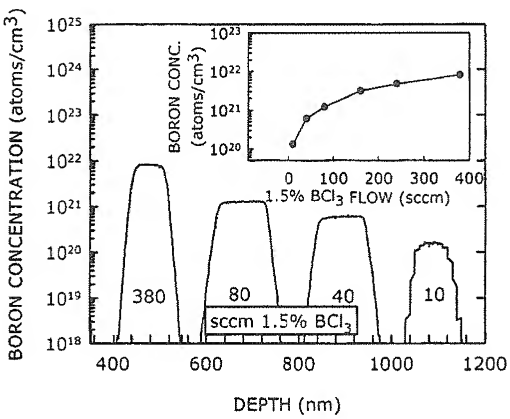


FIG. 1. Boron SIMS concentration depth profile for a typical modulation-doped sample. The film was deposited at 400 mTorr, 550 °C, and gas flows were 500 sccm SiH_4 and 700 sccm He, in addition to the 1.5% BCl_3 shown. Inset shows concentrations vs BCl_3 flow for the same conditions.

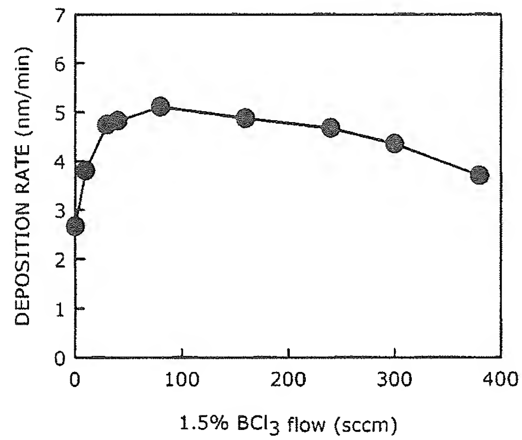


FIG. 2. Average deposition rate of boron-doped silicon films on SiO_2 substrates as a function of 1.5% BCl_3 flow. The films were deposited at 400 mTorr, 550 °C, and gas flows of 500 sccm SiH_4 and 700 sccm He, in addition to the 1.5% BCl_3.

heating using five independently controlled heating element coils outside of the quartz pressure vessel. The deposition temperature was 550 °C, the pressure was 400 mTorr, and the gas flows consisted of 500 sccm of SiH_4, 700 sccm of helium (He), and various flows of 1.5% BCl_3 (balance He). Helium was used to mix the two other gases and improve film thickness and sheet resistance (R_s) uniformity. Thicknesses of deposited films were measured by ellipsometry on nine points on the wafer, cross-sectional scanning electron microscopy (SEM), or transmission electron microscopy (TEM). TEM was performed at an accelerating voltage of 300 keV using both bright- and dark-field conditions. X-ray diffraction (XRD) spectra were collected by a Bragg–Brentano diffractometer using Cu $K\alpha$ radiation and a diffracted beam monochromator. Sheet resistance (R_s) was measured using a four-point probe on 49 points on the as-deposited silicon films. Sheet resistance nonuniformity averaged 6% (3 sigma). Sheet resistance nonuniformity was better with the use of BCl_3 compared to B_2H_6 as dopant gas source.[12] Boron concentration depth profiles were measured by secondary ion mass spectrometry (SIMS) using a 3 keV O_2^+ ion beam to detect ^{11}B, or by Auger electron spectroscopy (AES) microprobe using a beam energy of 20 keV, a current of 10 nA, and a tilt of 30° normal to the sample. The SIMS analysis area is a 75 μm×75 μm square in the middle of a 200 μm×200 μm sputter crater. The SIMS extracted boron concentration is the average found in the 75 μm ×75 μm area. The error in concentration for SIMS analysis is estimated to be ±20% of the total dose. The area of analysis for AES was 40 nm in diameter, with a sampling depth of 7.5 nm within that area. The error in concentration for AES analysis was estimated to be 1 at. %. Boron concentrations were calibrated by implant standards of known dose and energy. Sputter cleaning of silicon films for AES analysis was done *in situ* by 5 keV Ar^+ at a incident angle 55° to sample normal, and a current of 1 μA.

The amount of boron incorporated into the silicon film was controlled by the flow of BCl_3 gas. To establish how boron doping concentration varied with BCl_3 flow, films of silicon were deposited with BCl_3 gas flows modulated during deposition to produce doping "spikes." Figure 1 shows a typical SIMS concentration depth profile of a BCl_3 modulation-doped film deposited on a SiO_2 substrate. During deposition, the gas flow of SiH_4 was held constant, while flows of BCl_3 and He were varied to create the dopant spikes. For the first 40 min after the wafer had stabilized at deposition temperature and pressure, only SiH_4 was flowed to deposit undoped Si. Dopant was then introduced by flowing BCl_3 and 700 sccm of He. Undoped silicon 100 nm thick was deposited in between the dopant spikes by interrupting the flow of BCl_3 and He. This process was repeated several times with different flows of BCl_3 to provide the final modulation-doped film. The same technique was repeated for different BCl_3 flows to build a database of boron concentrations for given BCl_3 flows. The data are summarized in the inset in Fig. 1.

III. RESULTS

A. Deposition rate

The deposition rates for ~200 nm thick films as a function of BCl_3 flow on silicon dioxide substrates (constant flows of SiH_4 and He) was measured (Fig. 2). The deposition rate is the calculated average for the 200 nm thick film. With low flows of BCl_3, the deposition rate curve is similar to those produced by SiH_4/B_2H_6 and Si_2H_6/B_2H_6 source gases: The deposition rate increases with increasing flow of dopant gas flows until a maxima is reached.[6,8,12] This observation indicates that the accelerated deposition rate is dependent on the concentration of boron and not on the particular boron source gas.

B. X-ray diffraction

Undoped silicon films deposited by SiH_4 gas source on SiO_2 substrates at low pressure have been found to be amorphous or mostly amorphous at deposition temperatures of

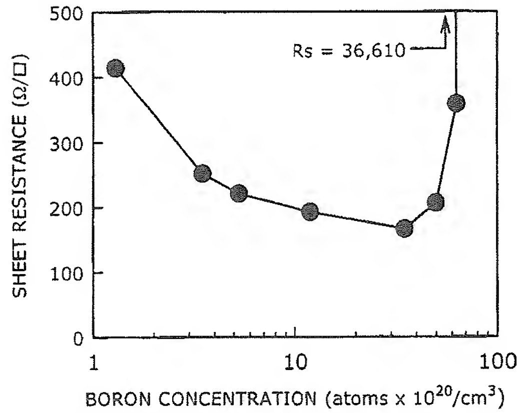


FIG. 3. Sheet resistance vs. boron concentration for ~200 nm Si films deposited on oxide substrates. The films were deposited at 400 mTorr, 550 °C, and gas flows were 500 sccm SiH_4 and 700 sccm He. The flow of 1.5% BCl_3 was adjusted for each film to produce the doping concentration shown.

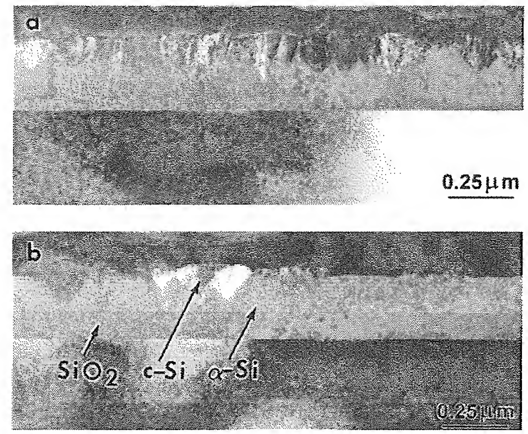


FIG. 5. Cross-sectional TEM image (dark field) of silicon films deposited on oxide for 40 min at 400 mTorr, 550 °C, and gas flows of 500 sccm SiH_4, 700 sccm He, and BCl_3 flows to produce average doping concentration (a) $5.0\pm 1.0\times 10^{21}/cm^3$ and (b) $8.2\pm 1.6\times 10^{21}/cm^3$.

550 °C and less.[1,11] Incorporation of a significant amount of boron induces polycrystalline deposition instead of amorphous at deposition temperatures of 550 °C and below.[12,13] The crystallinity of 200 nm thick BCl_3-doped silicon films deposited at 550 °C with various boron concentrations was examined by XRD (Fig. 3). A trend of increasing crystallinity is observed with increasing boron concentration. However, the film with a boron concentration $8.3\pm 1.6\times 10^{21}/cm^3$ did not exhibit pronounced XRD peaks. The absence of diffraction peaks does not necessarily imply that the films are completely amorphous, as will be shown in the TEM results.

C. Sheet resistance

The sheet resistance of ~200 nm thick silicon films deposited on oxide substrates with various boron concentrations deposited at 550 °C and 400 mTorr on oxide substrates was measured (Fig. 4). While the decrease in R_s with increasing boron concentration up to $3.1\pm 0.6\times 10^{21}/cm^3$ is expected, the sharp increase in R_s for boron concentrations in excess of $3.1\pm 0.6\times 10^{21}/cm^3$ is not intuitively expected. Similar sheet resistance phenomena in heavily boron-doped silicon films deposited by SiH_4/B_2H_6 in an ultrahigh vacuum chemical vapor deposition chamber (~1 mTorr) at 550 °C was observed by Lin *et al.*[10]

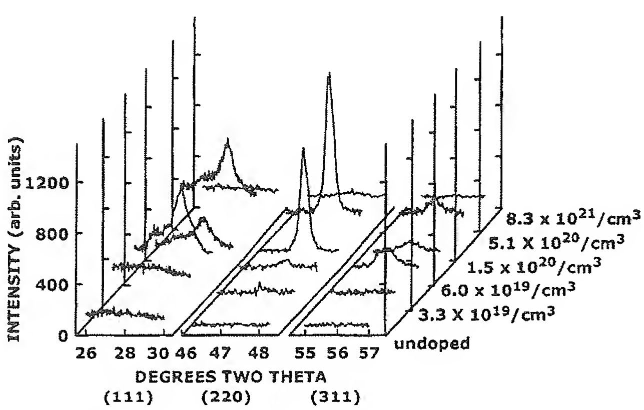


FIG. 4. XRD spectra of boron-doped silicon films *as deposited* on oxide substrates. The films were deposited at 400 mTorr, 550 °C, and gas flows were 500 sccm SiH_4 and 700 sccm He. The flow of 1.5% BCl_3 was adjusted for each film to produce the doping concentration shown in (sample with highest concentration had a range of boron concentrations depending on the depth in the film; the average concentration is shown).

D. Transmission electron microscopy

The morphology of very highly doped films was examined in TEM. Cross-sectional images of ~200 nm thick silicon films deposited on SiO_2 with a boron concentrations in excess of $3.1\pm 0.6\times 10^{21}/cm^3$ had amorphous and polycrystalline components [Figs. 5(a) and 5(b)]. The inverted pyramid shapes were determined by electron selected area diffraction to be silicon grains, and the smooth film that surrounds them was amorphous. The images show the fraction of the film that is amorphous increases with increasing boron concentrations in excess of $3.1\pm 0.6\times 10^{21}/cm^3$ [Fig. 5(b)]. The amorphous silicon is 136 nm thick and has a smooth surface, while the top of the silicon grains are approximately 200 nm above the oxide substrate and have rougher surfaces. The deposition time for the sample shown in Fig. 5(b) was 40 min, and so the deposition rate for the amorphous component is 3.4 nm/min. The silicon grains coalesce with longer deposition times. When the same conditions were used to deposit a film for 80 min, the surface of the film was continuous polysilicon (Fig. 6), while the amorphous phase was beneath the polysilicon surface.

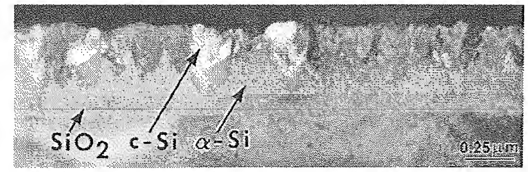
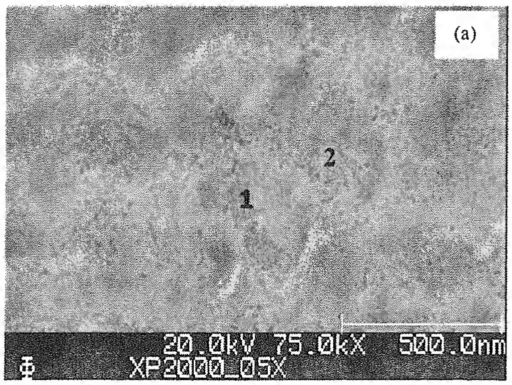


FIG. 6. Cross-sectional TEM image (dark field) of silicon film deposited on oxide for 80 min at 400 mTorr, 550 °C, with gas flows of 500 sccm SiH_4, 700 sccm He, and BCl_3 flow to dope the film to an average concentration of $8.1\pm 1.6\times 10^{21}/cm^3$.



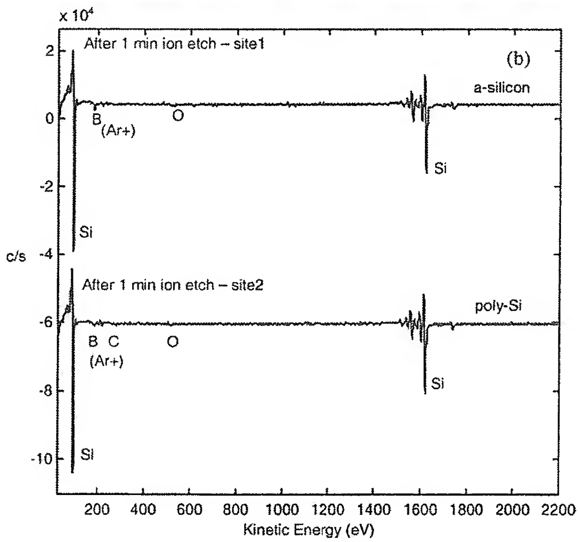


FIG. 7. SEM image (a) and AES spectra (b) of the surface of a boron-doped silicon film deposited for 40 min while flowing 180 sccm of 1.5% BCl_3. The extracted boron concentration of the amorphous area marked by a "1" in the SEM image is 12 ± 1 at. % ($6.6\pm0.6\times10^{21}/cm^3$), and the polycrystalline area marked by a "2" in the SEM image is 8 ± 1 at. % ($4.4\pm0.6\times10^{21}/cm^3$).

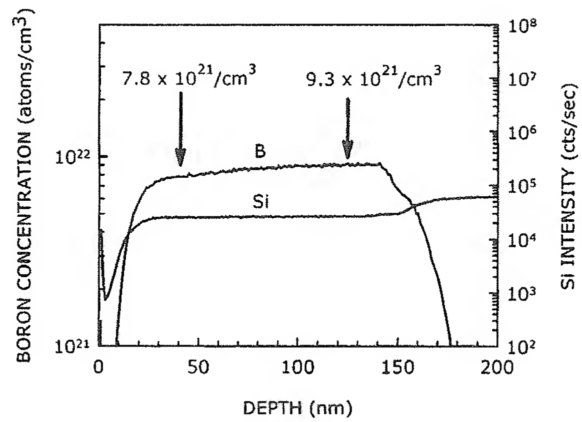


FIG. 8. SIMS spectra of the silicon film deposited on oxide for 40 min at 400 mTorr, 550 °C, with gas flows of 500 sccm SiH_4, 700 sccm He, and 380 sccm 1.5% BCl_3.

E. Secondary ion mass spectrometry and Auger electron spectroscopy

The surface of the sample in Fig. 5(b) was examined more closely by AES microprobe. A scanning electron microscope integrated with the AES microprobe shows the regions of analysis in Fig. 7(a). Figure 7(b) shows the amorphous silicon region (smooth) had a measured boron concentration of 12 ± 1 at. % ($6.6\pm0.6\times10^{21}/cm^3$), while the crystalline silicon region (rough) had a measured boron concentration of 8 ± 1 at. % ($4.4\pm0.6\times10^{21}/cm^3$) and have a lower boron concentration. The silicon grains are growing more rapidly and have a lower boron concentration than the amorphous silicon. The silicon grains are not only growing more rapidly than the amorphous silicon. While the image was sufficient to distinguish the smooth amorphous regions from the rougher polycrystalline regions, grain boundaries could not easily be distinguished in the SEM image used to select the region from which to collect the AES spectra. As a result, AES information collected from the polycrystalline region included both grains and grain boundaries. As grain boundaries can accommodate larger concentrations of dopant than grains, even larger lateral boron concentration gradients may exist in the polycrystalline analysis region.

Confirmation that boron concentration changes with crystallinity of the film is provided by concentration depth profile analysis analysis of the sample shown in Fig. 5(b). The boron concentration depth profile changes from $7.8\pm1.6\times10^{21}/cm^3$ at the surface, which is about half amorphous and half polycrystalline as shown by the TEM image, to $9.3\pm1.9\times10^{21}/cm^3$ near the oxide surface where the film is almost completely amorphous (Fig. 8). The polycrystalline phase, which is predominant at the surface of the film, has a lower boron incorporation relative to the amorphous phase, which is dominant near the oxide interface. The SIMS and AES measures of boron concentrations in the polycrystalline versus amorphous silicon phases are in general agreement.

IV. DISCUSSION

From the data, it is evident that when the boron reaches a critical concentration during silicon deposition, lateral phase separation into amorphous and polycrystalline components occurs. The silicon grains share a similar inverted pyramid shape and protrude above the amorphous silicon matrix. The grains nucleate on what appear to be point sources on the oxide substrate, and then grow upward and outward with continued deposition. Protrusion of the silicon grains above the amorphous matrix is caused by a faster vertical growth rate for the grains relative to the amorphous phase. The inverted pyramid shape of the grains implies a lateral growth of the grains that is also faster than the vertical growth rate of the amorphous film.

The increasing amorphous fraction of the film with increasing boron concentration accounts for the increase in sheet resistance (Fig. 3) and the decrease in XRD intensity (Fig. 4) when boron concentration exceeds $3\times10^{21}/cm^3$. The density of grain nucleation sites decreases as boron concentration exceeds $3\times10^{21}/cm^3$ as shown by the TEM images. The AES-measured boron concentration of $4.4\pm0.6\times10^{21}/cm^3$ for the silicon grains approximately coincides

with the boron concentration ($3.1 \pm 0.6 \times 10^{21}/cm^3$) at the R_s minimum shown in Fig. 3, showing that as the boron concentration exceeds $3-4 \times 10^{21}/cm^3$, a portion of the film is deposited amorphous. The amorphous phase not only has a higher boron concentration than the polycrystalline phase as shown by the AES and SIMS measurements (Figs. 7 and 8), but the boron concentration continues to increase in the amorphous phase with increasing BCl_3 flows, while the boron concentration polycrystalline phase does not change as the BCl_3 flow is increased.

V. CONCLUSION

A deposition mechanism for the films deposited on oxide consistent with all the empirical observations is now presented. As the boron incorporation exceeds $3.1 \pm 0.6 \times 10^{21}/cm^3$ on SiO_2, silicon and boron deposition can no longer organize into coherent grains and the film is amorphous. Very highly boron-doped silicon films are largely amorphous at the beginning of deposition, but contain crystal nuclei. The silicon grains grow via a different catalysis, with a lower boron concentration and a higher growth rate than the surrounding amorphous silicon. Polycrystalline silicon can incorporate a maximum boron concentration of $3-4 \times 10^{21}/cm^3$ (8 at. %) on SiO_2 for the deposition conditions examined in this article. The density of silicon grains is inversely proportional to the amount of BCl_3 flowed during film deposition. The fast growth rate of the silicon grains relative to the amorphous silicon causes the eventual coalescence of the grains with longer deposition times. Even for films deposited with very large boron concentrations, which are initially mostly amorphous, with continued deposition the grains will coalesce and result in fully polycrystalline film surfaces. As the grains grow together the film has a uniformly lower boron concentration than if it is growing with a combination of amorphous and polycrystalline regions.

ACKNOWLEDGMENT

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Low Resistivity p^+ Polycrystalline Silicon Deposition at Low Temperatures with SiH_4/BCl_3

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The deposition of p^+ polycrystalline silicon films on SiO_2 substrates by SiH_4/BCl_3 gases has been characterized. Films were deposited at temperatures as low as 460°C with an as-deposited resistivity of $3560 \pm 130\ \mu\Omega$ cm with good step coverage in oxide trenches. The extracted activation energy for silicon deposition was 0.6 eV for temperatures between 490 and 580°C and boron concentration of $2.0 \pm 0.4 \times 10^{21}/\text{cm}^3$, compared with 0.2 eV for p^+ silicon deposition by SiH_4/B_2H_6 for similar conditions. Silicon films deposited by SiH_4/BCl_3 are polycrystalline with low resistivities as-deposited at 460°C, whereas films deposited by SiH_4/B_2H_6 are amorphous at deposition temperatures <520°C.
 [DOI: 10.1149/1.1691531]

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Heavily doped silicon films have many applications for integrated circuits (ICs); as gates, line resistors, and local interconnects in complementary metal oxide semiconductor (CMOS) transistors, and as sources, channels, and drains in thin film transistors.[1,2] By doping the silicon film *in situ*, the need for ion implantation and associated process steps is minimized. Silicon films can be deposited as amorphous, single crystal, or polycrystalline (polysilicon). When *in situ* doped films are deposited amorphous, they must be annealed at temperatures in excess of 550°C to crystallize the film, to activate the dopant(s), and obtain a low resistivity film. However, this elevated anneal temperature makes film formation incompatible for many temperature-sensitive IC applications. Such applications include polysilicon-based thin film transistors for liquid crystal displays, where the devices are deposited on glass substrate.[3] A wider range of glass substrates becomes available with decreased process temperature, and if decreased enough, enables polysilicon deposition on plastic substrates.[4] The recent development of polysilicon-based devices that can be stacked on top of one another has increased the desire for low-temperature deposition.[5,6] Polysilicon deposition temperature of less than 475°C is one enabling factor for the use of low resistivity aluminum interconnects between the polysilicon devices, instead of more thermally stable but higher resistivity materials like $TiSi_2$ or tungsten.[7] The ability to deposit doped polysilicon films at low temperatures with a low resistivity as deposited is therefore desirable.

Typically, polysilicon films are deposited at temperatures in excess of 500°C to maintain high deposition rates and therefore high wafer throughput. However, p-type dopant gases have been shown to increase the deposition rates of silicon compared to undoped or n-type dopant gases.[8,9] *In situ* p^+-doped polysilicon can be deposited with various source gases. The most widely used p-type doping source for silicon is diborane, B_2H_6.[10-13] Diborane and silane gases can deposit silicon films with boron dopant concentrations greater than 1×10^{21} B/cm^3, with low, as-deposited resistivities reported at deposition temperatures of 520°C.[10] However, at deposition temperatures less than 520°C, p^+ silicon films deposited with SiH_4/B_2H_6 gases are amorphous as-deposited, and require a second, higher temperature anneal (>550°C) to transform them into low resistivity states. A second drawback of B_2H_6 as a p-type source gas is the nonuniformity of the boron distribution across wafers in batch furnaces at deposition temperatures that produce polycrystalline silicon. Low-pressure chemical vapor deposition (LPCVD) of silicon is typically done in large batch-type furnaces that hold 50 or more wafers to achieve high per wafer throughput and low cost. The boron concentration has been shown to vary from $1 \times 10^{21}/\text{cm}^3$ to greater than $6 \times 10^{21}/\text{cm}^3$ for a 65 wafer (150 mm diam) batch in a horizontal furnace deposited with and SiH_4/B_2H_6 gases at a temperature of 550°C.[12] This nonuniformity is not acceptable for large volume production. The nonuniformity of the dopant distribution can be reduced by using disilane (Si_2H_6) gas with B_2H_6 and reducing the deposition temperature to 350°C: boron concentration nonuniformity of 10% was achieved for a 100 wafer (150 mm) batch.[12] However, at a deposition temperature of 350°C, films deposited with Si_2H_6/B_2H_6 were amorphous as-deposited, and required post deposition anneal at 600°C to obtain low resistivity. Disilane (Si_2H_6) is also more expensive than silane.

We have characterized the properties of p^+ silicon films deposited using SiH_4/BCl_3 source gases. Of particular interest is the ability to deposit doped crystalline silicon films on large wafer batches at temperatures as low as 460°C with reasonable deposition rates and low resistivity as-deposited. The deposition rate, boron concentration, sheet resistance variance with deposition temperature, and step coverage in trench structures are described, with emphasis on low-temperature properties.

Experimental

Silicon films were deposited on 200 mm silicon wafers with 100 nm of thermally grown SiO_2. The deposition tool was a vertical furnace capable of holding 80 wafers with a pitch of 8.6 mm in a quartz boat. The boat was rotated and a full load of wafers was maintained during each deposition. Deposition uniformity was achieved by using five independently controlled heating element coils outside of the quartz pressure vessel and by using multiple gas injectors. Thickness was measured by ellipsometry on five points on the wafer. Sheet resistance (Rs) was measured using a four point probe on 49 points on the as-deposited films. Boron concentration depth profiles were measured by secondary ion mass spectrometry (SIMS) using a 3 keV O_2^+ ion beam to sputter. The error in concentration for SIMS analysis was estimated to be ±20% of the total dose. Step coverage of p^+ polysilicon films was evaluated on wafers with various trench widths etched into 1 μm thick oxide films. The aspect ratio of the trenches varied from 2.9 to 5.0.

To establish how the doping concentration varies with temperature, a single film of silicon was deposited with temperature and gas flows modulated during deposition to produce doping "spikes." The film was deposited at a pressure of 400 mTorr and an initial temperature of 580°C, and the gas flows were 500 sccm SiH_4, 700 sccm He, and 10 sccm of 1.5% BCl_3 (bal. He). Helium was used to mix the reactive gases and improve film thickness and sheet resistance (Rs) uniformity. After deposition of the initial boron-doped "spike" at 580°C, 1.5% BCl_3 and He gas flows were discontinued in order to deposit undoped silicon. After depositing approximately 150 nm of undoped silicon, the flow of SiH_4 was then discontinued, halting

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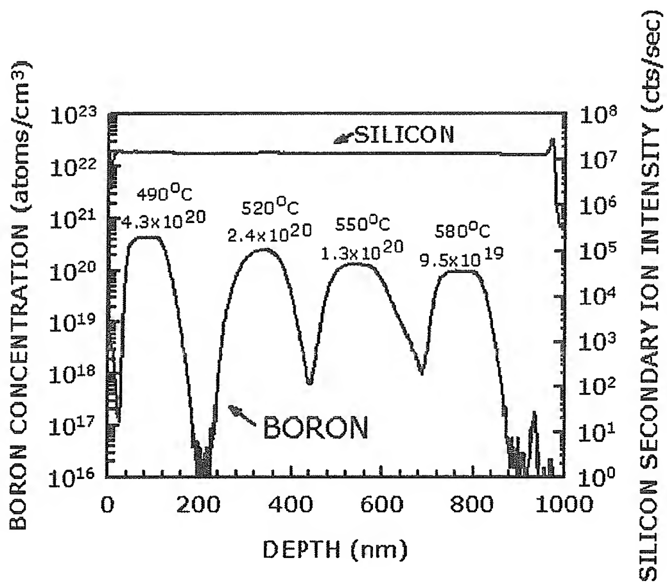

Figure 1. Boron SIMS concentration depth profile for a typical temperature modulation-doped polysilicon film. The film was deposited at 400 mTorr and gas flows of 500 sccm SiH_4, 10 sccm 1.5% BCl_3 (bal. He), and 700 sccm He. The deposition temperature of each "spike" and the boron concentration (B/cm^3) is noted in the graph.

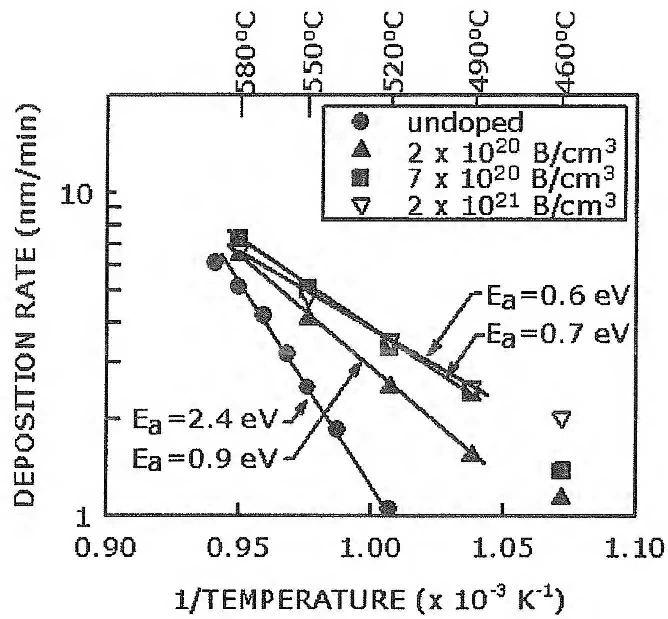

Figure 2. Steady-state deposition rates (after incubation time) of p^+ polysilicon films with various concentrations of boron. Films were deposited on SiO_2 substrates at 400 mTorr, with 500 sccm SiH_4 and 700 sccm He. The flow of 1.5% BCl_3 (bal. He) was varied with each deposition.

deposition, and the flow of He restarted to maintain pressure at 400 mTorr. The temperature was then reduced to 550°C and the wafers were allowed to equilibrate at the new temperature for 60 min in the He ambient. Silane and boron trichloride gas flows were restarted after temperature equilibration at 550°C to produce a second boron-doped "spike," followed again by undoped silicon deposition. The entire process was repeated at temperatures of 520 and 490°C. In this way the concentration of boron was determined with different deposition temperatures for the same gas flows in one film. The same technique was repeated for different flows of 1.5% BCl_3 at deposition temperatures between 460 and 580°C to build a library of boron concentrations with 1.5% BCl_3 gas flows at different deposition temperatures.

Results and Discussion

Figure 1 shows the boron SIMS concentration depth profile for a spike film on an oxide wafer. The concentration of boron in the silicon films increased as temperature is decreased. We believe that the decreasing boron concentration is due to enhanced desorption of boron or boron species from the surface. A similar effect has been found in *in situ* phosphorus-doped silicon deposition.[14] The steady-state deposition rates of several p^+ polysilicon films with different doping concentrations at different temperatures are shown in Fig. 2, and are compared with the undoped silicon deposition rate. Similar to B_2H_6, the addition of BCl_3 dopant gas increases the deposition rate relative to undoped silicon.[10-12] At a flow of 500 sccm SiH_4, a pressure of 400 mTorr, and a deposition temperature of <520°C, the deposition rate of undoped silicon is low enough to make undoped silicon deposition economically unfeasible for thick films. However, deposition rates of 1-2 nm/min at a temperature of 460°C for boron-doped silicon films are still practical for manufacturing purposes.

The activation energies for silicon deposition are shown in Fig. 2. Activation energies of 0.6-0.9 eV for polysilicon deposition by SiH_4/BCl_3 at temperatures between 490 and 580°C were extracted, with the value dependent on doping concentration (lower energy for higher concentrations). The decreasing activation energy suggests that higher flows of BCl_3 facilitates the adsorption of SiH_4 onto the wafer surface.[10] In comparison, a value of 0.2 eV was extracted for amorphous p^+ silicon film deposition using SiH_4/B_2H_6, deposited at 450-525°C and 350-410 mTorr pressure.[10] Doping velocity, which is defined as the product of the deposition rate and boron incorporation, is plotted for the SiH_4/BCl_3 depositions in Fig. 3. The doping velocity remains relatively constant through the temperature regime, suggesting that the rate limiting step for the reaction is gas diffusion in the furnace in the range 460-580°C. In contrast, deposition by SiH_4/B_2H_6 was shown to be diffusion-limited at temperatures above 500°C, and surface reaction rate-limited at temperatures less than 500°C, as indicated by a change in doping velocity at that temperature.[12] For SiH_4/B_2H_6, improved boron concentration uniformity of silicon films across a batch of wafers was achieved by

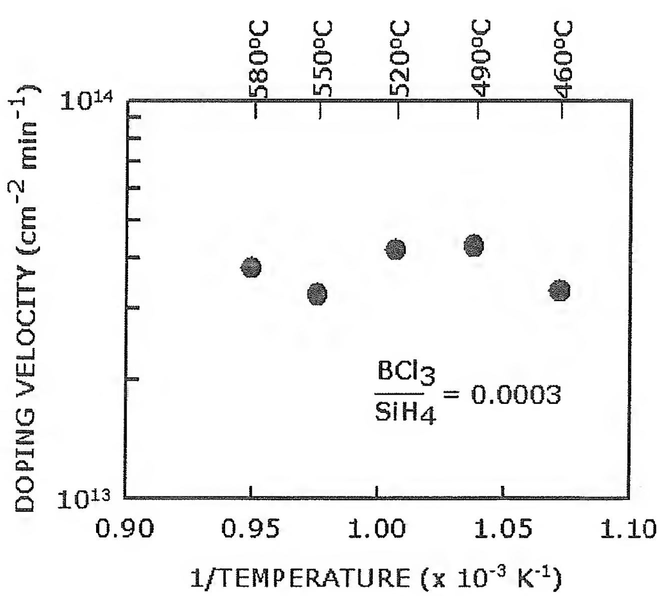

Figure 3. Doping velocity for one mixture of SiH_4/BCl_3. The film was deposited at 400 mTorr and gas flows of 500 sccm SiH_4, 10 sccm 1.5% BCl_3 (bal. He), and 700 sccm He.

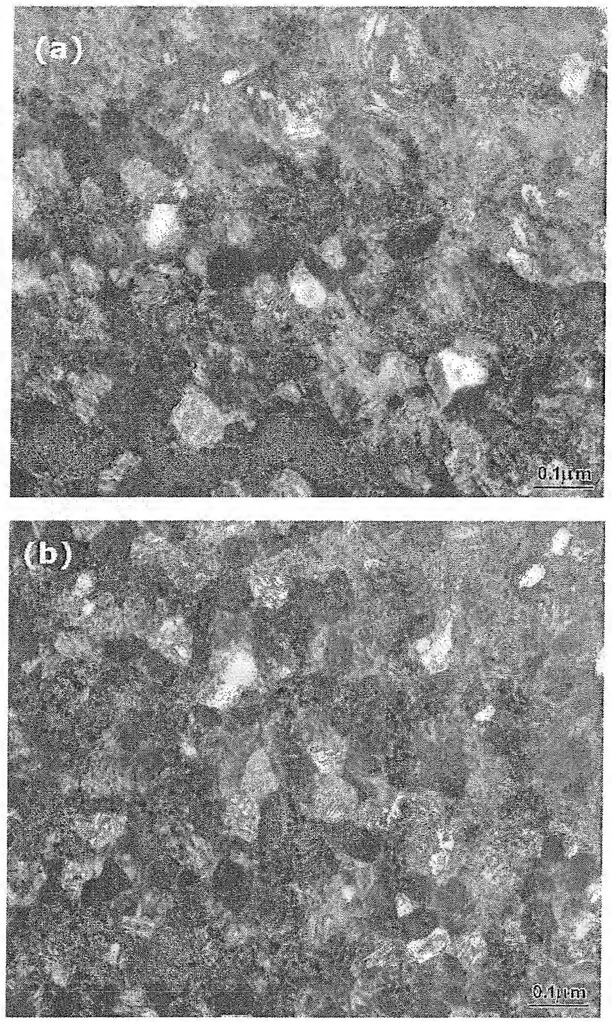

Figure 4. Weak beam, dark field TEM micrographs of 200 nm thick p^+ polysilicon films. Films were deposited on SiO_2 substrates at 400 mTorr, with 500 sccm SiH_4, and 700 sccm He. The flow of 1.5% BCl_3 (bal. He) was controlled to produce doping concentrations of (a) 2 ± 0.4 × 10^{20} B/cm^3, and (b) 2 ± 0.4 × 10^{21} B/cm^3.

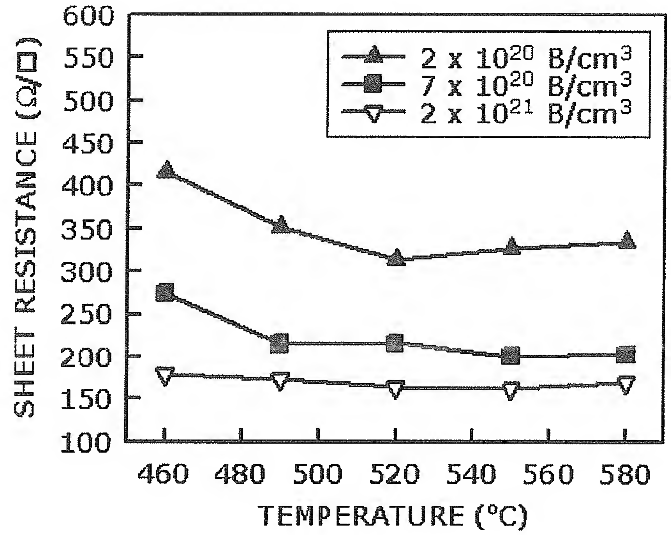

Figure 5. As-deposited sheet resistances of 200 nm thick p^+ polysilicon films deposited at varying deposition temperatures. Sheet resistance was measured by 4 point probe on 49 points on each wafer. Films were deposited on SiO_2 substrates at 400 mTorr, with 500 sccm SiH_4, and 700 sccm He. The flow of 1.5% BCl_3 (bal. He) was varied with each deposition.

reducing the deposition temperature to less than 500°C. The improved uniformity was attributed to the change to surface reaction limited regime from diffusion limited. At temperatures greater than 500°C, the fast reaction of SiH_4 + B_2H_6 caused B_2H_6 to be depleted with increasing distance from the injector, resulting in boron concentration nonuniformity across a batch of wafers. Although SiH_4/BCl_3 deposition is diffusion-limited for the range 460-580°C, the higher activation energy and slower reaction rate prevents BCl_3 from being depleted within the diffusion length of the furnace. And, critically, silicon deposited by SiH_4/BCl_3 remains polycrystalline with low resistivity for a deposition temperature of 460°C, where SiH_4/B_2H_6 deposits amorphous silicon for temperatures <520°C.

Good dopant distribution inside a vertical batch furnace using SiH_4 and BCl_3 source gases enabled 60 silicon wafers (200 mm) per deposition at 460°C with a within-wafer (wafer-to-wafer) thickness nonuniformity of 2.6% (3.1%) 1σ, and a sheet resistance within-wafer nonuniformity of 2.8% (16.1%) 1σ as-deposited. The grain size of polysilicon films deposited by SiH_4/BCl_3 is characterized to compare to films deposited by SiH_4/B_2H_6. Using the line-intercept technique on transmission electron micrographs (Fig. 4) of films deposited from SiH_4/BCl_3, the grain size for the 2 × 10^{20}/cm^3 (2 × 10^{21}/cm^3) doped film is estimated to be 52 nm (53 nm), with a one sigma variation of 21 nm (25 nm). These grain sizes are similar for polysilicon films deposited with SiH_4/B_2H_6 at 600°C with similar boron concentrations.[15]

The films deposited for this study have the expected decrease in sheet resistance with increasing boron concentrations (Fig. 5). It has been shown previously that increasing boron concentrations above 2.0 × 10^{21}/cm^3 will not necessarily result in a decreasing resistivity of the as-deposited films due to amorphous phase formation.[16] A similar phenomenon has been found in polysilicon films deposited at very low pressures (1 mTorr) using SiH_4/B_2H_6.[17] Hence, we have limited the boron concentrations in this study to 2 × 10^{21}/cm^3 or less. We extracted resistivities of 3220 to 3560 µΩ cm for the films with the highest boron concentration (2.0 ± 0.4 × 10^{21}/cm^3) at deposition temperatures 460-580°C. This range of resistivities does not reflect a consistent trend with temperature. Table I shows the theoretical resistivities of single crystalline silicon compared with that measured in the p^+ polysilicon films deposited at 520°C in this study for equivalent carrier and doping concentrations, respectively.[18] The as-deposited resistivities are far higher than theoretically predicted. This higher resistivity is due to a small fraction of the dopant is being active, and a relatively low charge carrier mobility caused by grain boundaries and other crystal defects that are scattering centers.[18]

Despite rough film surfaces, the step coverage on wafers with topography was excellent, with substantially the same thickness film on trench sidewalls as on the horizontal surface for the 460°C depo-

Table I. Resistivities of single crystal silicon compared with p^+ polysilicon films in this study. Polysilicon films were deposited at 520°C.

	Resistivity (calculated, µΩ cm) for single crystal Si with carrier concentration	Resistivity (measured, µΩ cm) for p^+ polysilicon with metallurgical concentration
2 × 10^{20}/cm^3	600	6260
7 × 10^{20}/cm^3	170	4320
2 × 10^{21}/cm^3	100	3260

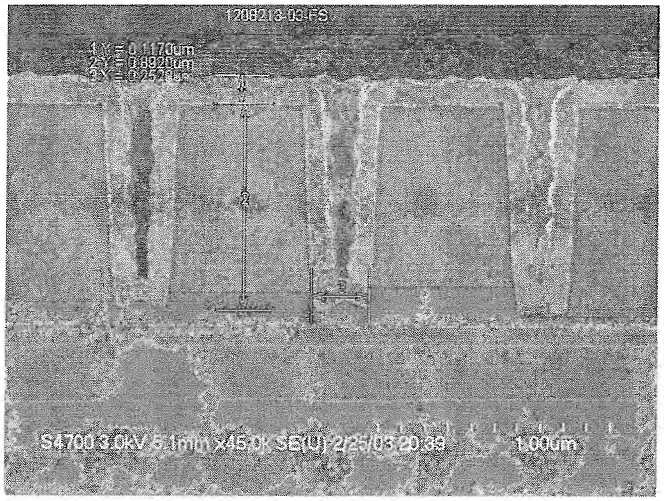

Figure 6. Step coverage of p^+ polysilicon film in 3.7:1 aspect ratio trench as shown by cross-sectional SEM micrograph. Film was deposited at 460°C, 400 mTorr with doping concentration $2.0 \pm 0.4 \times 10^{21}$ B/cm^3.

sition temperature with $2.0 \pm 0.4 \times 10^{21}$/cm^3 boron doping (Fig. 6). These partially filled trenches show that the film has nucleated evenly on the sidewalls through the depth of the trench. Even smaller width trenches with higher aspect ratios were completed filled by the film deposition. This highly doped film has been used to fill similar trenches to make vertical interconnects between vertically stacked polysilicon devices.[3] The films deposited with lower concentrations of boron and at higher deposition temperatures had similar step coverage in trenches (not shown).

Conclusion

Highly p^+-doped polysilicon films can be deposited at temperatures as low as 460°C with good thickness and doping uniformity for a 60 wafer load in a vertical batch furnace with low resistivities as-deposited. The activation energy for deposition using SiH_4/BCl_3 was found to be 0.6 and 0.9 eV for boron doping concentrations 2.0 ± 0.4 and $0.2 \pm 0.04 \times 10^{21}$/cm^3, respectively, in the temperature range 490 to 580°C. Step coverage of the p^+ polysilicon films in oxide trenches remained excellent at low temperature.

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